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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to an acrylic syrup constituent.

[0002]

[Description of the Prior Art]An epoxy resin, an acrylic resin, etc. are known as resin used for paint covering of road surfaces, such as concrete and asphalt, or a floor line. However, the impasto by 1 time of coating is difficult for an epoxy resin, and it is inferior to endurance in it. There is a fault, like a cure rate becomes slow and execution time becomes long.

[0003]On the other hand, although the impasto in 1 time of coating is possible, and cure time is short and being excelled in endurance, a hardened material colors it yellow temporally, and the acrylic syrup resin indicated to JP,1-36508,B etc. is in the tendency for weatherability to be insufficient. This acrylic syrup as a polymerization initiator made to polymerize Diacyl peroxide (benzoyl peroxide). It is thought that it originates in the system which consists of a tertiary amine (for example, dimethylp-toluidine) containing at least one piece the aromatic group coupled directly with the nitrogen atom being used.

[0004]Although the yellow allochroism of a hardened material is suppressed and it is generally possible to lessen the quantity of a polymerization initiator, i.e., the loadings of an aromatic tertiary amine, for improving weatherability, if loadings are lessened, the rate of polymerization of acrylic syrup will be reduced, non-polymerization monomers increase, and the fall of physical properties is caused. Although making the amount of combination polymer increase and reducing monomer component loadings is also considered, if many polymer is blended, the viscosity of a system will rise remarkably and will spoil workability. In order to lower the viscosity of a system, the molecular weight of the polymer to blend needed to be lowered, but when the molecular weight was low, there was a problem that the intensity of an acrylic syrup hardened material fell remarkably.

[0005]

[Problem(s) to be Solved by the Invention]This invention solves the problem of this conventional technology, and an object of this invention is to provide the acrylic syrup constituent which can be used for obtaining acrylic resin system road marking and the constituent for floor coating which reduced yellow allochroism.

[0006]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, as a result of advancing examination wholeheartedly, by using a specific acrylic syrup constituent, this invention persons found out that the above-mentioned purpose could be attained, and resulted in this invention.

[0007]Namely, at least one sort as which this invention was chosen from (A) acrylic ester and methacrylic acid ester, (B) A methacrylic-acid-ester system macro monomer meltable to an ingredient (A), and copolymerizable, (C) Be in an acrylic syrup constituent containing a polymerization initiator which becomes an ingredient (A) from a meltable plasticizer, a compound which has at least two polymerization nature combination in one molecule (D) and the (E) peroxide, and a tertiary amine.

[0008]

[Embodiment of the Invention]In the constituent of this invention, as the acrylic ester used as an ingredient (A), and methacrylic acid ester, For example, methyl acrylate, ethyl acrylate, acrylic acid n-butyl, Acrylic ester, such as acrylic acid t-butyl and 2-ethylhexyl acrylate phenol EO denaturation acrylate, Methyl methacrylate (it may be hereafter written as MMA.), ethyl methacrylate, N-butyl methacrylate, methacrylic acid i-butyl, t-butyl methacrylate, Lauryl methacrylate, 2-ethylhexyl methacrylate, tridecyl methacrylate, Stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, Methacrylic acid 2-hydroxyethyl, 2-hydroxypropyl methacrylate, Methacrylic acid ester, such as dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, glycidyl methacrylate, tetrahydrofurfuryl methacrylate, and methacrylic acid allylphenol EO denaturation methacrylate, is mentioned. The mixture of methyl methacrylate and 2-ethylhexyl acrylate whose T_g of a homopolymer is 0 ° or less whose glass transition temperature (henceforth T_g) of a homopolymer is not less than 80 ° is suitably used also in these.

[0009]The acrylic syrup constituent of this invention sets and, as for the content ratio of an ingredient (A), it is preferred that it is the range of 30 - 80 weight section to total quantity 100 weight section of an ingredient (A) - an ingredient (C). By making the content ratio of an ingredient (A) into 30 % of the weight or more, this is because it is in the tendency for the coating workability of a constituent to become good and is in the tendency for polymerization curing nature to become good by considering it as 80 or less % of the weight.

[0010]Next, in the constituent of this invention, it is required for an ingredient (A) to be soluble

or a thing to distribute as a methacrylic-acid-ester system macro monomer used as an ingredient (B). What has an AKUROIU (meta) group or a styryl group is suitably used for an ingredient (A) and a copolymerizable piece end.

[0011]How to rank second and make [carries out anionic polymerization of 1, the MMA, etc., and] it react to a containing halogen (meta) AKUROIU compound as a production means of the methacrylic-acid-ester system macro monomer of an ingredient (B) for example. How to carry out the radical polymerization of the MMA etc., rank second under existence of 2 and mercaptoacetic acid, and make it react to glycidyl group content (meta) acrylic ester. The group transfer polymerization of the MMA etc. is carried out by using 3 and a trimethylsiloxy ethyl trimethylsilyl JIMECHIRUKETEN acetal as an initiator, and it ranks second and can obtain easily by the method of making it react to AKUROIU (meta) chloride, etc.

[0012]As a monomer used for such a methacrylic-acid-ester system macro monomer, For example, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, methacrylic acid i-butyl, t-butyl methacrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, etc. are mentioned. A copolymer with a desirable monomer with low Tg of the polymer and methyl methacrylate, and polymer of methyl methacrylate, for example, n-butyl methacrylate, methacrylic acid i-butyl, 2-ethylhexyl methacrylate, and lauryl methacrylate, etc. are mentioned.

[0013]the molecular weight of the methacrylic-acid-ester system macro monomer used as an ingredient (B) in the constituent of this invention -- a number average molecular weight -- 3000-100000 -- desirable -- 5000-70000 -- it is a thing of the range of 10000-50000 still more preferably.

[0014]As for the content ratio of an ingredient (B), in the acrylic syrup constituent of this invention, it is preferred that it is the range of 1 - 60 weight section to total quantity 100 weight section of an ingredient (A) - an ingredient (C). This is because it is in the tendency for the cure time of a constituent to be shortened by making the content ratio of an ingredient (B) into 1 % of the weight or more and is in the tendency for the coating workability of a constituent to become good by considering it as 60 or less % of the weight. It is the range of 15 to 50 weight section preferably. Since the addition of a polymerization initiator can also be decreased while being able to decrease an ingredient (A), maintaining good physical properties by using this ingredient (B), it becomes possible to reduce yellow coloring of a hardened material.

[0015]In the constituent of this invention, as a meltable plasticizer for the ingredient (A) used as an ingredient (C), For example, dibutyl phthalate, di-n-octyl phthalate, di-2-ethylhexyl phthalate, Octyldodecyl phthalate, di-n-decyl phthalate, di-isodecyl phthalate, Phthalic ester, such as butylbenzyl phthalate, a di-2-ethylhexyl horse mackerel peat, An octyldidecyl horse mackerel peat, di-2-ethylhexyl sebacate, Dibutyl sebacate, di-2-ethylhexyl sebacate, a polypropylene glycol, Epoxy system polymeric plasticizers, such as a polyester plasticizer of a chlorinated paraffin, an adipic acid system, an azelaic acid system, a sebacic acid system, and

a phthalate system, epoxidized oil, and epoxidation fatty acid ester, etc. are mentioned. These mix one sort or two sorts or more, and are used.

[0016]These plasticizers are added for the purpose of improvement in the imitation nature to the road surface by viscosity regulation of the acrylic syrup constituent of this invention, or plasticization of a hardened material. As for the using rate, when the total quantity of an ingredient (A) - an ingredient (C) is made into 100 weight sections, it is preferred to consider it as the range of 0.1 - 25 weight section. By making the content ratio of an ingredient (C) into 25 or more weight sections, the resistance to contamination of a hardened material is in the tendency which becomes good. It is the range of five to 20 weight section more preferably.

[0017]In the acrylic syrup constituent of this invention, an ingredient (D) is a compound which has at least two polymerization nature combination in one molecule, and is an ingredient added in order to raise the endurance of a hardened material when hardening. As for the quantity, it is preferred to consider it as the range of 0.1 - 50 weight section to total quantity 100 weight section of an ingredient (A) - an ingredient (C). By making content of an ingredient (D) into 50 or less weight sections, the pliability of a hardened material is in the tendency which becomes good.

[0018]As an example of an ingredient (D), for example Ethylene glycol di(metha)acrylate, 1, 2-propyleneglycol di(meth) acrylate, 1, 3-butylen glycol di(metha)acrylate, Alkane JIORUJI (meta) acrylate like 1,6-hexanediol di(metha)acrylate, Diethylene GURIKORUJI (meta) acrylate, dipropylene GURIKORUJI (meta) acrylate, Polyoxoalkylene GURIKORUJI (meta) acrylate, such as triethylene glycol di(metha)acrylate, tetraethylene glycol di(metha)acrylate, and poly ethylene glycol di(metha)acrylate, and divinylbenzene are mentioned. These are independent or are used by two or more sorts of concomitant use.

[0019]In the constituent of this invention, the polymerization initiator used as an ingredient (E) consists of a peroxide and a tertiary amine. As a peroxide, benzoyl peroxide is used suitably. Benzoyl peroxide is an inactive fluid or solid, in order to avoid the danger on handling, and it is preferred to use what that was diluted by about 50% of concentration is [being paste state or] powdered. The rate of a peroxide is the range of 0.5 - 5 weight section preferably 0.2 to 10 weight section among the acrylic syrup constituent of this invention to total quantity 100 weight section of an ingredient (A) - an ingredient (D).

[0020]As a tertiary amine, an aromatic thing is preferred and especially N,N'-dimethylaniline, One sort or two sorts or more of combination of N,N'-dimethyl- p-toluidine, N,N'-JI (hydroxyethyl)-p-toluidine, and N,N'-JI (hydroxypropyl)-p-toluidine are preferred. The rate of the tertiary amine in an acrylic syrup constituent of this invention is the range of 0.3 - 3 weight section preferably 0.1 to 5 weight section to total quantity 100 weight section of an ingredient (A) - an ingredient (D).

[0021]The acrylic syrup constituent of this invention can be stiffened within 2 hours with the

combination of a compound in a -30 ** -50 ** temperature requirement.

[0022]At least one sort of the paraffin which has the melting point of not less than 40 ** in the acrylic syrup constituent of this invention for the purpose of the air shutoff operation under hardening reaction in a paint film surface, grant of the gloss on the surface of hardening, and improvement in dirt-proof nature, and a wax can be added. As paraffin or a wax, higher fatty acid, such as paraffin wax, polyethylene wax, stearic acid, 1, and 2 hydroxystearic acid, etc. are mentioned, for example. As for this paraffin or wax, it is preferred to use it in the range of 0.1 - 5 weight section to total quantity 100 weight section of an ingredient (A) - an ingredient (D).

[0023]The endurance of adhesive strength with the adhesive stabilization and the bulking agent to a ground the making it improve purpose in the acrylic syrup constituent of this invention Gamma-methacryloxypropyl trimethoxy silane, Silane coupling agents, such as gamma-glycidioxypropyltrimethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, and gamma-mercapto propyltrimethoxysilane, can be added.

[0024]In order to stabilize the hardenability of the constituent of this invention Tributyl phosphite, Tri (2-ethylhexyl) phosphite, tridecyl phosphite, Tristearylphosphite, tris (nonylphenyl) phosphite, Various kinds of defoaming agents and leveling agents for the purpose of preparing the surface appearance of a coat for phosphite, such as triphenyl phosphite, A polymerization retarder like hydroquinone, hydroquinone monomethyl ether, and 2,4-dimethyl- t-butylphenol can be added in order to raise the storage stability of the constituent of this invention.

[0025]Although coating is generally presented with the constituent of this invention as a compound mixed with aggregate and other bulking agents, as aggregate, oil absorption has [25cc linseed oil / following / 100g] mean particle diameter preferred at not less than 10 micrometers. As these aggregate, rock powder, such as sand, silicon sand, quartz sand, a thing that colored these or a calcinated thing, quartz powder, and silicon sand powder, the colored porcelain, the thing that carried out calcination hardening and pulverized the earthenware base, a zinc white, calcium carbonate, alumina, a glass bead, etc. are mentioned. It is desirable because of the improvement of coating workability and self-leveling nature in the combination of the aggregate in which particle diameter differs in use.

[0026]Silica powder like Aerosil as a bulking agent for giving thixotropy to a compound, etc. can also be added. As a bulking agent, out of the above, it is preferred to use a color pigment and a color, for example, titanium oxide, barium sulfate, carbon black, Chrome Vermilion, red ochre, ultramarine, cobalt blue, copper phthalocyanine blue, Phthalocyanine Green, etc. are used. Generally, to constituent 100 weight section of this invention, these blend the range of zero to 900 weight section as a bulking agent, and present coating with it.

[0027]Although the compound which mixed bulking agents, such as an additive agent and

aggregate, with the constituent of this invention is used for covering of the floor line of concrete, asphalt, a steel plate, etc., or a wall surface, After performing priming to grounds, such as a floor line and a wall surface, if needed when constructing, it is preferred to carry out coating of this mixture on it.

[0028]As an execution method, methods, such as a spray method, trowel finishing, brush coating, and roller coating, can be used. Or it does not mix aggregate, before carrying out coating of the compound which only the part mixed beforehand and hardening it, the execution method which makes some aggregate project to a paint film surface, and gives nonslip nature to it is also possible by sprinkling aggregate.

[0029]In the compound which mixes aggregate beforehand, the kind and quantity of aggregate are chosen according to the purpose of coating. According to the execution methods, such as a spray, brush coating, and roller coating, can construct a comparatively thin coat, i.e., a 0.2-1-mm coat, but. It is preferred to make the amount of aggregate into the range of 30 to 100 weight section to constituent 100 weight section of this invention on the occasion of the combination to such a purpose. When constructing a thicker coat, i.e., a 1-30-mm coat, trowel finishing is preferred, and as for the amount of aggregate, it is preferred to consider it as the range of 100 to 900 weight section to constituent 100 weight section of this invention. In this case, when aiming at a smooth paint film surface, it is preferred to make the amount of aggregate few to about 100 weight sections, and it is preferred to make [many / to about 900 weight sections] the amount of aggregate from an economic viewpoint to thicken thickness of a coat. However, since the hardenability of a compound worsens, the amount of the amount of aggregate used exceeding 900 weight sections is not preferred.

[0030]According to an execution method, the constituent of this invention can also be used as a 2 liquid type (base resin and hardening agent).

[0031]

[Example]Although an example and a comparative example are given and this invention is explained hereafter, this invention is not restricted at all by these. The "part" under explanation expresses a weight section.

[0032]The valuation method in an example and a comparative example is as follows.

[Molecular weight] It measured using the gel permeation chromatography.

The [the degree of yellow (YI)] After cutting the obtained hardened material to 2.5-mm thickness and 10x20 mm, it measured with the spectrum analyzer.

[Flexural strength] It measured by tensilon / DTM-1-2500 (made by TOYO BALDWIN).

[0033][Related Example(s)] (manufacture of the MMA macro monomer which has a methacryloyl group at the piece end)

Under dry argon, in a 400-ml anhydrous tetrahydrofuran (THF) 5.6 g (20mmol) of trimethylsiloxy ethyl trimethylsilyl JIMECHIRUKETEN acetals, 0.06 g (0.23mmol) of tris

dimethylamino SURUFATORIMECHIRUSHIRUBI fluoride ($\text{TAS}^+(\text{CH}_3)_3\text{SiF}_2^-$) was added, and also dry MMA200g (2.0 mol) was dropped, and it was made to polymerize at 0 °C for 3 hours. Subsequently, the obtained polymer was added into 6 l. of liquid containing chloride, methanol washed settlings, and vacuum drying was carried out at 150 °C for 12 hours. 180g of polymethylmethacrylate (poly MMA) which has a hydroxyl group as a result at the piece end of number average molecular weight (M_n) =11000, weight-average-molecular-weight (M_w) =12100, and M_w/M_n =1.10 was obtained (90% of yield).

[0034]Obtained poly MMA90g (amount of hydroxyl groups 8.5mmol) was dissolved in 450-ml anhydrous THF, 2.02 g (20.0mmol) of trityl amine and 2.1 g (20.0mmol) of chloridation methacryloyl were added, and it was made to react at a room temperature for 24 hours. The reactant was added into 10 l. of methanol, methanol washed the sediment, and vacuum drying was carried out at 50 °C for 12 hours. 80g of MMA macro monomers which have a methacryloyl group at the piece end as a result were obtained (90% of yield). When the introduction rate of the methacryloyl group to an end was measured by NMR, it was 93%. Tg measured from differential scanning line thermometric analysis (DSC) was 102 °C.

[0035]

[Example 1]

Methyl methacrylate 40 copies 2-ethylhexyl acrylate Five copies Octyldecyl phthalate Ten copies Polypropylene-glycol dimethacrylate Five copies Paraffin wax (melting point: 45-65 °C) The mixture which consists of one copy is warmed at 50 °C, After adding a little MMA macro monomers [every 40 copies of] which have a methacryloyl group at the piece end obtained by the reference example and making it dissolve in it, agitating, it cooled to the room temperature. Then, agitation mixing of 0.42 copy of dimethylp-toluidine was added and carried out. Then, 0.7 copy of benzoyl peroxide was added, and when it constructed so that it might be promptly set to about 3 mm in thickness on a polyethylene terephthalate (PET) film after churning, it hardened by about 30 minutes after benzoyl peroxide addition at 20 °C. The hardened material was almost transparent. It was 4.1 when the yellow index (henceforth YI value) which shows the index of the degree of yellow of a hardened material was measured.

[0036][Example 2] The thing of M_w =35000 was used as an MMA macro monomer, and also the acrylic syrup constituent was stiffened on the same conditions as Example 1.

[0037]

[Comparative example 1]

Methyl methacrylate 55 copies 2-ethylhexyl acrylate Five copies Octyldecyl phthalate Ten copies Polypropylene-glycol dimethacrylate Five copies Paraffin wax (melting point: 45-65 °C) The mixture which consists of one copy is warmed at 50 °C, After having added a little poly MMA [every 25 copies of] of M_w =40000, making it dissolve and cooling to a room temperature, agitating, agitation mixing of 0.6 copy of dimethylp-toluidine was added and

carried out. Then, one copy of benzoyl peroxide was added, and when it constructed so that it might be promptly set to about 3 mm in thickness on a PET film after churning, it hardened by about 30 minutes after benzoyl peroxide addition at 20 **. YI value of the hardened material was 20.2.

[0038]

[Comparative example 2]

Methyl methacrylate 40 copies 2-ethylhexyl acrylate Five copies Octyldecyl phthalate Ten copies Polypropylene-glycol dimethacrylate Five-copy paraffin wax (melting point: 45-65 **) The mixture which consists of one copy is warmed at 50 **, After having added a little poly MMA [every 40 copies of] of Mw=12000, making it dissolve and cooling to a room temperature, agitating, agitation mixing of 0.42 copy of dimethylp-toluidine was added and carried out. Then, 0.7 copy of benzoyl peroxide was added, and when it constructed so that it might be promptly set to about 3 mm in thickness on a PET film after churning, it hardened by about 30 minutes after benzoyl peroxide addition at 20 **. YI value of the hardened material was 8.3.

[0039][Comparative example 3] Changed into poly MMA, and MMA / n-butyl methacrylate copolymer of Mw=73000 were used, and also the acrylic syrup constituent was stiffened on the same conditions as the comparative example 1.

[0040]As mentioned above, the presentation of the syrup of each example and a comparative example and the evaluation result after construction were collectively shown in Table 1.

[0041]

[Table 1]

	シラップ組成							評価結果	
	MMA (部)	多官能モノマー (部)	アクリレートモノマー (部)	可塑剤 (部)	ポリマー (部)	BPO (部)	DMPT (部)	YI値	強度 (kg/cm ²)
実施例1	40	5	5	10	ポリマー1 40	0.7	0.42	4.1	600
実施例2	40	5	5	10	ポリマー2 40	0.7	0.42	5.0	670
比較例1	55	5	5	10	ポリマー3 25	1.0	0.6	20.2	590
比較例2	40	5	5	10	ポリマー4 40	0.7	0.42	8.3	11
比較例3	55	5	5	10	ポリマー5 25	1.0	0.6	18.7	510

パラフィンワックス (融点: 45~65℃): 「実施例1~2」、「比較例1~3」に1重量部添加

[0042]The abbreviation name in Table 1 is as follows.

MMA: methyl methacrylate Polyfunctional monomer: Polypropylene-glycol dimethacrylate

Plasticizer : Octyldecyl phthalate acrylate monomer: 2-ethylhexyl acrylate Polymer 1 : Piece end methacrylic group macro monomer (Mw=12100)

Polymer 2 : Piece end methacrylic group macro monomer (Mw=35000)

Polymer 3 : Polymethylmethacrylate (Mw=40000)

Polymer 4 : Polymethylmethacrylate (Mw=12000)

Polymer 5 : Copolymer of MMA and n-butyl methacrylate (60/40, Mw=73000)

BPO : benzoyl peroxide DMPT : Dimethylp-toluidine[0043]

[Effect of the Invention]By having blended the methacrylic-acid-ester system macro monomer, the acrylic syrup constituent of this invention can be used for the use of a road marking agent and a floor coating agent, and can be used as intensity and the hardened material excellent in yellow-proof allochromism.

[Translation done.]